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Technical note

CATHODIC REDUCTION OF OXYGEN AND HYDROGEN PEROXIDE ON PLATINUM, PALLADIUM AND IRIDIUM SMOOTH ELECTRODES

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University of Milano (Italy)
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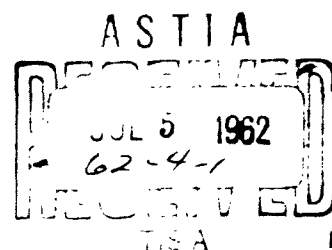
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ABSTRACT

Polarization curves in aci·', neutral and alkaline solutions have been drawn by potentiostatic method, for oxygen and hydrogen peroxide reduction processes and for hydrogen peroxide oxidation process, on Platinum, Iridium and Palladium electrodes.

These curves could be classified as follows : those whose slopes are 0.030 to 0.12, and those with slopes higher than 0.12. The former can be explained through already proposed mechanisms (addition of one electron or one atom of hydrogen to an adsorbed oxygen molecule; or addition of one electron to a HO_2 adsorbed radical) which mechanisms imply that the adsorption process is so quick as not to result kinetically determining. The latter involve a slow oxygen or HO_2 radicals adsorption which becomes kinetically determining first of all for Iridium in both acid and neutral solutions. For Palladium in H_2SO_4 solution and for Platinum in HCl solution the oxygen adsorption process is very slow essentially due to the complexing action of the solution with resulting formation of surface complexes which engage the metal atoms, thus preventing or reducing the formation of adsorbed oxide.

1. INTRODUCTION

Platinum has been used longer than other metals in researches on electrochemical behaviour of oxygen and hydrogen peroxide, both in the form of smooth plate and of platinum black.

These researches concern :

a) - Catalytic decomposition of hydrogen peroxide solutions, that is, according to GERISCHER's conclusions (1), an electrochemical process resulting from partial cathodic and anodic processes of reduction of hydrogen peroxide to water and of oxidation of hydrogen peroxide to oxygen. BIANCHI and his co-workers (2) have shown that decomposition of hydrogen peroxide in the case of acid solutions involves the adsorbed oxides of the metal.

b) - Anodic evolution of oxygen from hydrogen peroxide solutions and "depolarizing" action on anodic processes. These researches are owed to RIUS and OCON, RIUS and GUILLEN, HICKLING and WILSON,GINER, and BIANCHI and co-workers (3).

c) - Oxygen cathodic reduction process, which is strictly connected to hydrogen peroxide decomposition and reduction processes. Besides HOAR's researches (4) and ROITER and JAMPOLSKAJA's (4) mention must be made of the researches carried out by TOMASHOV, KRASIL'SHCHIKOV and ANDREIEVA, BIANCHI and RIVOLTA, BOCKRIS and OLDFIELD, GERISCHER, WINKELMANN, BIANCHI and CAPRIOGLIO, KRASIL'SHCHIKOV (4).

Researches on Pd and Ir are very few. Catalytic action of these metals on decomposition of hydrogen peroxide acid solutions has been considered by BIANCHI and co-workers (5), who here again have confirmed the intervention of the oxides.

Oxygen reduction on palladium has been glimpsed upon by BAIN (6); the case of iridium has been considered by BAIN (6) and by

GARRISON and LILLY (7).

In the case of platinum the various workers have confirmed that for oxygen cathodic reduction, polarization curves have 0.11 + 0.12 slope in the case of acid solutions, and 0.036 + 0.045 in the case of alkaline solutions (8).

These results have not been confirmed by KRASIL'SHCHIKOV and ANDREIEVA (9) in the case of platinum. By operating at extremely low current densities (ranging about 1 micro A/sqcm), they have checked a 0.59 slope in polarization curves, in both alkaline and acid solutions.

Hydrogen peroxide cathodic reduction has been examined only for platinum by GERISCHER (10) and WINKELMANN (11).

As it is well known, it runs over more negative potentials than theoretical potentials (1.77 Volts in acid solution and 0.88 Volts in alkaline solution).
Hydrogen peroxide cathodic reduction occurs at potentials which are very close to those observed for oxygen cathodic reduction (12).

Electrochemical reduction processes of oxygen and hydrogen peroxide may interfere in reduction processes of the oxides adsorbed on the electrode surface. For these latter processes the electro-chemical conditions of formation and reduction and the chemical stability conditions in contact with hydrogen peroxide solutions must be considered.

As far as platinum oxides are concerned, mention can be made of the researches made by HICKLING, VETTER and BERNDT, GINER, LAITINEN and ENKE, NAGEL and DIETZ, WILL and KNORR (13).
As it has already been shown by BIANCHI and CAPRIOGLIO (14), the potential for oxygen and hydrogen peroxide cathodic reductions in acid solutions is very close (about 0.8 V, NHS) to the one for the

system Pt-PtO.

The formation and red¹ ction of oxygen adsorbed on iridium have
been considered by KNORR and by BÖLD and BREITER (15).
As far as iridium oxides are concerned, only LATIMER's (16)
theoretical data are available. For palladium oxides HICKLING
and VRJOSEK's (17) experimental data are available.
As far as the chemical behaviour of oxides is concerned, it is
known that ~~water~~ H_2O_2 strongly reduces $Pt(OH)_2$ (18) and it reduces
with less strenght $Pd(OH)_2$ (19).
No data for iridium oxides are available.

2. - EXPERIMENTAL

The research which is matter of this report was carried out by
drawing polarization curves, concerning the electrode metals next
cited, by means of a potentiostat and a polarization cell already
described (20).
99,9% Iridium (Degussa), Platinum -10% Iridium, Platinum -20%
Iridium, 99,9% Platinum (Johnson and Matthey), 99,9% Palladium
(Johnson and Matthey) electrodes were considered. During the
above polarization experiments the following solutions were
employed, all of them prepared with reagent-grade Merck products:

Acid solutions : H_2SO_4 0.5M

Neutral solutions : Na_2SO_4 0.5M, H_3BO_3 0.5M and NaOH to
adjust pH at value 7.

Alkaline solutions : Na OH 0.1M and Na_2SO_4 0.5M

Hydrogen peroxide was added to the solutions so prepared until
the required concentrations were reached. Gases employed to
saturate and stir the above solutions during the measurements

were 99. 5% oxygen (with small traces of N_2 and rare gases), or
hyperpure nitrogen (99,999%) : these gases bubbled through the
solution in the cell at a rate of 150 cc/min. As reference electrode
a saturated-silver-chloride electrode was used : its own potential
value (+0. 196 V) then was added to the read potentials to convert
them into the normal hydrogen scale; no corrections were tried
for liquid junction potentials.

All the potentials indicated in the text and on the figures are intended
as referred to the normal hydrogen scale (NHS).

All the experiments were carried out with the aid of an air-
thermostat, at a temperature of $25 \pm 0,1^{\circ}$ C.

3. - EXPERIMENTAL RESULTS

In <u>alkaline solutions</u>, cathodic reduction of oxygen occurs without
remarkable overvoltages at potentials which are very close to those
of the process $O_2 + 2H^+ + 2e \longrightarrow H_2O_2$, and the resulting hydrogen
peroxide decomposes catalytically so that only some traces can be
determined in the solution ($\ll 10^{-4}$ M). The process runs in a
similar way (b=0. 060) on Platinum (Figure 1) and Palladium (Figure
2). In the case of Iridium (Figure 3) polarization curve has a stronger
slope (b=0. 12), although the same static potential and the same
limiting current are observed.

If the solution contains hydrogen peroxide (10^{-2} M) a cathodic
process and an anodic process are observed to which similar limiting
currents and potentials are corresponding, still very close to the
theoretical ones corresponding to the above reaction, considered
in terms of oxidation of hydrogen peroxide to oxygen.

Figure 4 shows the anodic and the cathodic polarization curve for
Platinum; and Figure 5 shows the very similar ones for Palladium.

Figure 6 shows the curves for Iridium, which although starting from the same static potentials and showing the same limiting currents, are divided into two parts. The first part is up to 0.5 micro A/cm^2, comparable to the curves for Platinum and Palladium (b = 0.020), and the next part with a greater slope (b = 0.060). In the case of neutral solutions, the cathodic reduction occurs for oxygen at a potential of about 500 mV (NHS) and is affected by intermediate overvoltages in the case of Platinum (Figure 7), Palladium (Figure 8) and Iridium (Figure 9). In the case of Palladium the slope is 0.060, while for Platinum the slope, initially similar to the one for Palladium, tends to increase with higher current densities. The slope is very greater for Iridium (b = 0.16).

The cathodic reduction and the anodic oxidation of hydrogen peroxide occurs at potentials close to 500 mV (NHS) as it is shown by the cathodic and the anodic polarization curve for Platinum (Fig. 10), Palladium (Fig. 11) and Iridium (Fig. 12). Still in this case cathodic overvoltages are small for Palladium (b = 0.020), medium for Platinum (b = 0.030) and very high for Iridium (b = 0.42). Anodic overvoltages are of the same order (b = 0.020 to 0.060) for the three metals.

In the case of acid solutions, the oxygen cathodic reduction clearly depends on the fact whether working with sulphuric or hydrochloric acid solutions, as Figure 13 shows. Polarization curves with Platinum electrode are little sloping with sulphuric acid solutions (b = 0.060) and the limiting currents are clearly observed. With hydrochloric acid solutions, the curves are strongly sloping (b = 0.180) and gradually join with the part to which the development of hydrogen is corresponding. The same thing happens with solutions containing hydrogen peroxide (Fig. 14).

The cathodic curve in a sulphuric acid solution (A) has a particular trend and clearly shows the limiting current, always keeping above

the curve obtained with an hydrochloric acid solution, which curve
(B) is strongly sloping and gradually connecting with the hydrogen
discharge. The anodic curve (C) has been determined only in
sulphuric acid solution (b = 0.080) and shows the same limiting
current as the cathodic curve.

Figure 15 shows the cathodic polarization curves for oxygen
reduction on Iridium in a sulphuric and in an hydrochloric acid
solution. It is observed that with Iridium the difference disappears
which had been observed with Platinum, and polarization curve is
however still very sloping (b = 0.28) and connected with the part
corresponding to the hydrogen cathodic discharge.

In the case of solutions containing hydrogen peroxide (Fig. 16) the
cathodic curves both in sulphuric and in hydrochloric acid solutions
remind those for Platinum, although a better nobility for Iridium
in the cathodic process with sulphuric acid solutions is only kept
for very small current densities. In sulphuric solutions, the
anodic curve offers a characteristic hysteresis : the slope in the
first part of the curve (b = 0.050) is comparable to the one for
Platinum. In the case of Pt 90-Ir 10 alloys (Figures 17-18) and
Pt 80-Ir 20 alloys (Figures 19-20), the same differences are
observed between sulphuric and hydrochloric acid solutions, as
those already observed for pure Platinum. In the case of Palladium
it is impossible to work in hydrochloric acid solutions, because of
the electrode corrosion. Oxygen cathodic reduction in a sulphuric
acid solution goes according to the curve shown on Figure 21,
being strongly sloping and gradually connected with the part corre-
sponding to the hydrogen discharge. Figure 22 shows the anodic
curve (b = 0.060) and the cathodic curve (b = 0,24), comparable
to those obtained for Platinum in a sulphuric solution of hydrogen
peroxide.

TABLE I

Slope of polarization curves

for $0.01 < i < 1 \text{ mA/cm}^2$, at $25°C$

			Platinum	Palladium	Iridium
Acid solutions — H_2SO_4	O_2	cathodic	0.060	0.24	0.28
	H_2O_2	anodic	0.080	0.060	0.050
		cathodic	0.030/0.45	0.24	0.040/0.34
Acid solutions — HCl	O_2	cathodic	0.180	-	0.28
	H_2O_2	cathodic	0.24	-	0.34
Neutral solutions	O_2	cathodic	0.060	0.060	0.16
	H_2O_2	anodic	0.060	0.060	0.040
		cathodic	0.030	0.030	0.42
Alkaline solutions	O_2	cathodic	0.060	0.060	0.12
	H_2O_2	anodic	0.030	0.020	0.030
		cathodic	0.020	0.030	0.060

TABLE II

Static potentials at $25°$ C

		Platinum	Palladium	Iridium
Acid solutions — H_2SO_4	O_2	0.92 V	0.77 V	0.90 V
	H_2O_2	0.79 V	0.78 V	0.85 V
Acid solutions — HCl	O_2	0.72 V	-	0.86 V
	H_2O_2	0.88 V	-	0.88 V
Neutral solutions	O_2	0.51 V	0.52 V	0.52 V
	H_2O_2	0.44 V	0.47 V	0.46 V
Alkaline solutions	O_2	0.20 V	0.21 V	0.23 V
	H_2O_2	0.10 V	0.11 V	0.15 V

4. - DISCUSSION

On considering Table 1 and Table 2, showing the experimental
results with Platinum, Palladium and Iridium, it is apparent that
polarization curve slope for <u>oxygen cathodic reduction</u> on Platinum
is 0. 060 in sulphuric acid solutions, for the field of current
densities examined in this work.

The same result is obtained for Platinum in alkaline and neutral
solutions, thus confirming Krasilshchikov's results already
cited [4]. Different results are obtained for Palladium in sulphuric
acid solution and Platinum in hydrochloric acid solution. In both
cases polarization curves have a high slope (0. 18 ÷ 0. 24), thus
implying a different mechanism for the oxygen cathodic reduction.
In the case of Iridium, polarization curves for oxygen cathodic
reduction in acid solution have a very high slope (0. 28), and this
higher slope is also observed in neutral (0. 16) and in alkaline
solutions (0. 12).

As far as <u>hydrogen peroxide</u> solutions are concerned, due account
is to be taken of the fact that hydrogen peroxide, particulary in
alkaline solutions, undergoes a decomposition and the potential
recorded on polarization curves is a mixed potential, resulting
from the cathodic reduction process of hydrogen peroxide to water,
and from the anodic oxidation process of hydrogen peroxide to oxygen.
The mixed potential of the hydrogen peroxide solutions is very close
to the reversible potential for the process

$$H_2O_2 - 2e \longrightarrow O_2 + 2 H^+$$
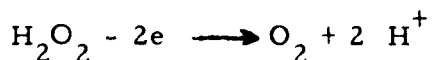
showing that the decomposition process is controlled by the hydrogen
peroxide reduction cathodic process.

In other words, all the cathodically reducible hydrogen peroxide
is spent in the decomposition process and then the cathodic external

polarizing current cannot correspond to the hydrogen peroxide cathodic reduction.

Cathodic and anodic polarization curves have a low slope (0.030 + 0.020) in both neutral and alkaline solutions, but the cathodic curve must be attributed to the reduction process of the oxygen which develops in the hydrogen peroxide decomposition.

In the sulphuric acid solutions where such decomposition is much smaller, there is less oxygen available for the cathodic process and the polarization curve slope on platinum is kept small only for limited values of current density (Fig. 14, A).

In the case of Palladium, for which polarization curve for oxygen cathodic reduction is strongly sloping (Fig. 21), even the cathodic curve for hydrogen peroxide solutions is very sloping (Fig. 22, B). This is also true for platinum in hydrochloric acid solutions (Fig. 13, B and 14, B).

As far as anodic behaviour is concerned, Iridium is analogous to Platinum and Palladium, except for the lower values of the limiting currents in acid solutions, which values were attributed, in a previous paper (21), to the lower reactivity of Iridium oxide with hydrogen peroxide solutions.

As far as the cathodic behaviour is concerned, polarization curve slopes are always higher, even in the alkaline solution themselves. As one single exception, there is a part in the curve at low current densities for solutions of hydrogen peroxide in sulphuric acid (Fig. 16, A).

In a hydrochloric acid solution, the behaviour of Iridium is analogous to Platinum, and to Gold in sulphuric solution (23).

Polarization curves obtained with Platinum, Palladium and Iridium can be divided into two main classes :

Those whose slopes are between 0.040 and 0.12, and those with slopes higher than 0.12.

The former can be explained through one of the mechanisms already described (addition of one electron or one atom of hydrogen to a molecule of adsorbed oxygen; or the addition of one electron to a HO_2 adsorbed radical), which mechanisms imply that the adsorption process is so quick as not to result kinetically significant. This is the case of Platinum in acid (H_2SO_4), neutral and alkaline solutions, of Palladium in neutral and alkaline solutions, and Iridium in alkaline solutions.

When the adsorption process is slow, as soon as it becomes kinetically significant, the interdependence of the potential and the current density will result through the coverage of the metal surface with adsorbed oxygen, and will involve a slope in the polarization curve that is generally high.

This is the case of Iridium for which it is to be concluded that oxygen adsorption processes are slow, in both acid and neutral solutions. For Palladium in sulphuric acid solutions and for Platinum in hydrochloric acid solutions the conclusion should be that the oxygen adsorption process is very slow, due to the complexing action of the solution and to the resulting formation of surface complexes which engage the atoms of the metal, thus preventing or reducing the formation of adsorbed oxide.

When, during the cathodic polarization, the surface coverage by adsorbed oxygen is nullified (22), the covering begins with atomic hydrogen and the cathodic process results from the discharge of hydrogen adsorbed atoms which combine with the oxygen dissolved in the solution (depolarization).

If the oxygen adsorption process is very slow - case of Iridium - the hydrogen discharge potential is reached before the limiting current for the reduction of oxygen, and the polarization curve joins with the part corresponding to the hydrogen discharge.

REFERENCES

(1) - H. GERISCHER - Z. fuer Phys. Chem. Neue Folge : <u>6</u>, 178 (1956)

(2) - G. BIANCHI, F. MAZZA and T. MUSSINI - Electrochimica Acta : submitted for publication

(3) - A. RIUS and J. OCON - Anales Real Soc. Espan. Fis. y Quim. : <u>B 41</u>, 38, (1945)

A. RIUS and J. M. GUILLEN - Anales Real Soc. Espan. Fis. y Quim. : <u>B 53</u>, 5, (1957)

A. HICKLING and W. H. WILSON - J. Electrochem. Soc. : <u>98</u>; 425, (1951)

V. J. GINER - Z. Elektrochem. : <u>64</u>, 491, (1960)

G. BIANCHI, G. CAPRIOGLIO, G. DAVOLIO, F. MAZZA and T. MUSSINI Chimica e Industria : <u>43</u>, 146, (1961)

(4) - T. P. HOAR - Proc. Roy. Soc. : <u>A 142</u>, 628, (1933)

ROITER and YAMPOLSKAYA : Acta Physicochim. USSR : <u>7</u>, 247, (1937)

N. D. TOMASHOV - Review in Light Metals : <u>11</u>, 388, (1948)

A. I. KRASILSHCHIKOV and V. A. ANDREIEVA - J. Phys. Chem. USSR: <u>27</u>, 389, (1953)

G. BIANCHI and B. RIVOLTA - Chimica e Industria : <u>36</u>, 358, (1954)

J. O!M. BOCKRIS and L. F. OLDFIELD - Trans. Faraday Soc. : <u>51</u>, 249, (1955)

H. GERISCHER - (cited)

D. WINKELMANN - Z. Elektrochem. : <u>60</u>, 731 , (1956)

G. BIANCHI and G. CAPRIOGLIO - Electrochimica Acta : <u>1</u>, 18, (1959)

A. I. KRASILSHCHIKOV - Soviet Electrochemistry, Consultants Bureau, New York 1961 - Vol. II, page 151.

(5) - G. BIANCHI, F. MAZZA and T. MUSSINI - (cited)

(6) - H. G. BAIN - Trans. Electrochem. Soc. : <u>78</u>, 173, (1940)

(7) - A. D. GARRISON and J. F. LILLY - Trans. Electrochem. Soc. : <u>65</u>, 275, (1934)

(8) - K.J. VETTER - Elektrochemische Kinetik, Berlin 1961, page 513

(9) - A.I. KRASILSHCHIKOV and V.A. ANDREIEVA - (cited)

(10) - H. GERISCHER - (cited)

(11) - D. WiNKELMANN - (cited)

(12) - G. BIANCHI - Corrosion et Anticorrosion : 5, 146, (1957)

(13) - A. HICKLING - Trans. Faraday Soc. : 41, 333, (1945)

G. RAEDLEIN - Z. Elektrochem; 61, 724 (1957)

K.J. VETTER and D. BERNDT - Z. Elektrochem. : 62, 378, (1958)

V.J. GINER - Z. Elektrochem. : 63, 386, (1959)

H.A. LAITINEN and C.G. ENCKE - J. Electrochem. Soc.: 107, 773,
(1960)

K. NAGEL and H. DIETZ - Electrochimica Acta : 4, 1, (1961)
                        Electrochimica Acta : 4, 141, (1961)

F.G. WILL and C.A. KNORR - Z. Elektrochem. : 64, 258, (1960)

(14) - G. BIANCHI and G. CAPRIOGLIO - (cited)

(15) - C.A. KNORR - Z. Elektrochem. : 64, 271, (1960)

W. BOELD and M. BREITER - Electrochimica Acta: 5, 169, (1961)

(16) - W.M. LATIMER - Oxidation Potentials, 2nd Edition, New York 1959,
page 218

(17) - A. HICKING and G.G. VRJOSEK - Trans. Faraday Soc. : 57, 123,
(1961)

(18) - GMELINS HANDBUCH - Platin, Teil C; Weinheim 1940, page 44

(19) - GMELINS HANDBUCH - Palladium; Berlin 1938; page 264

(20) - R. PIONTELLI, G. BIANCHI and co-workers, Z. Elektrochem. : 58,
86, (1954)

(21) - G. BIANCHI, F. MAZZA and T. MUSSINI - (cited)

(22) - F.G. WILL and C.A. KNORR - Z. Elektrochem. : 64, 270, (1960)

(23) - G. BIANCHI, F. MAZZA and T. MUSSINI - Technical Scientific Note n. 5
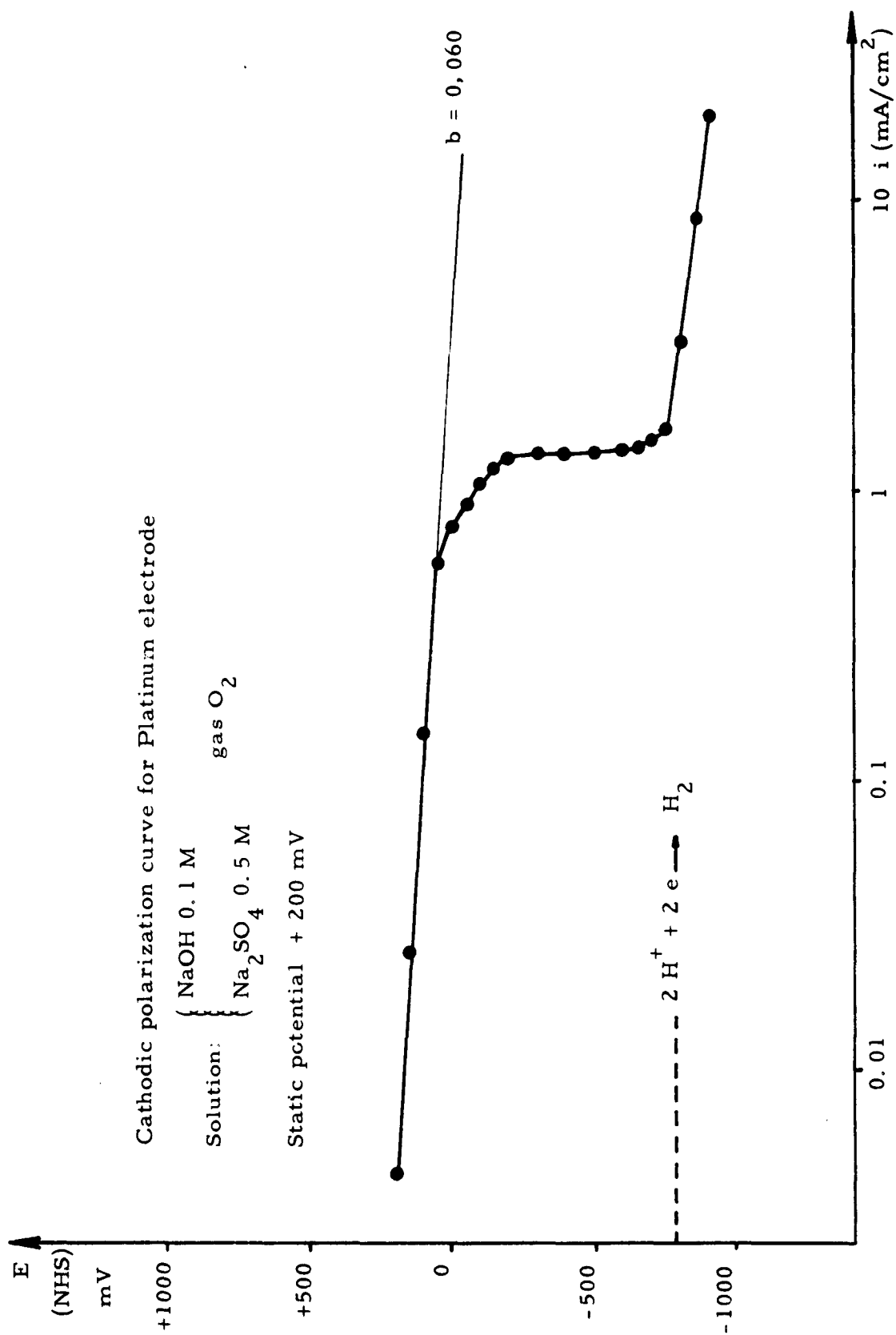Contract AF 61(052) - 260 (december 1961) - AFOSR 2054

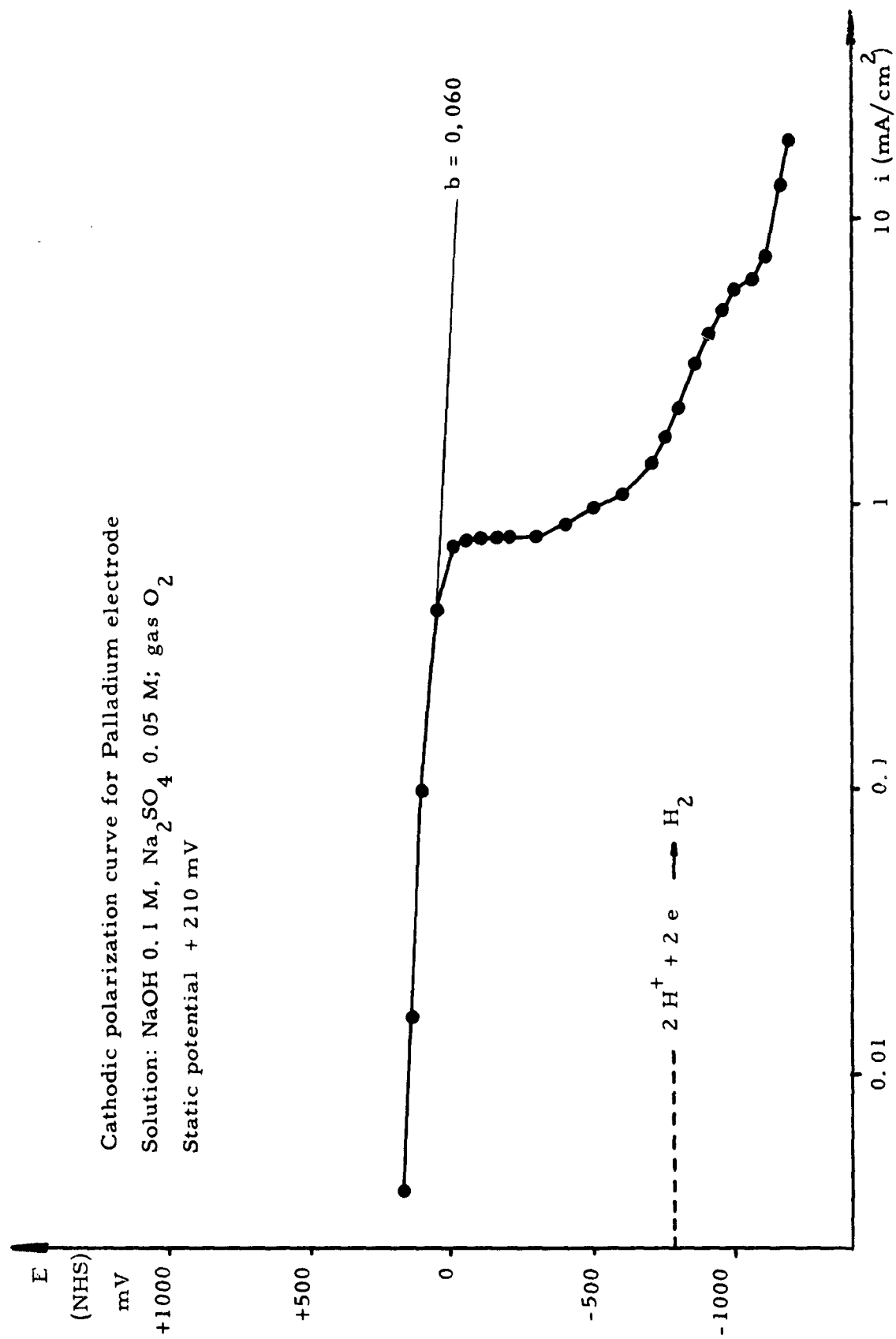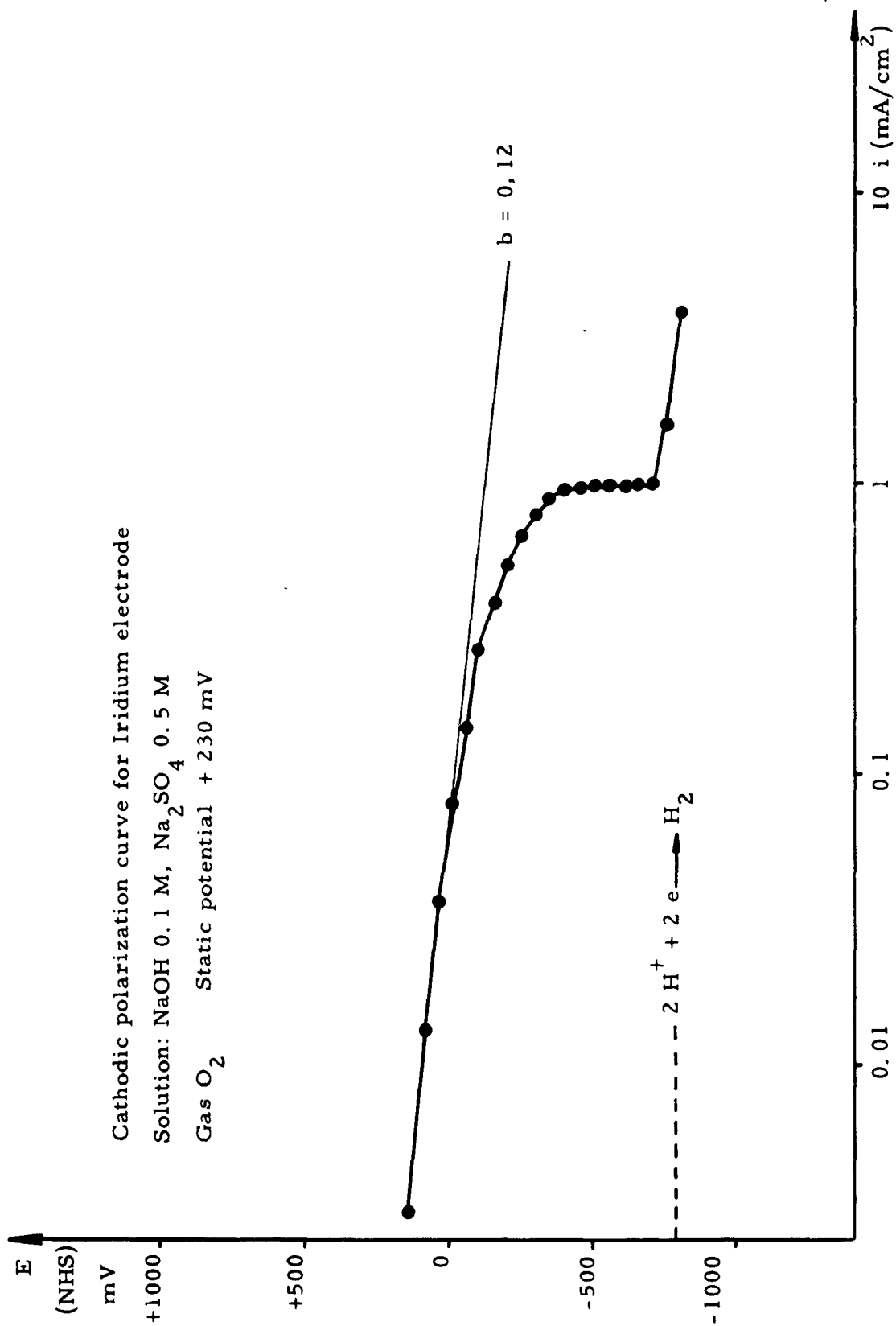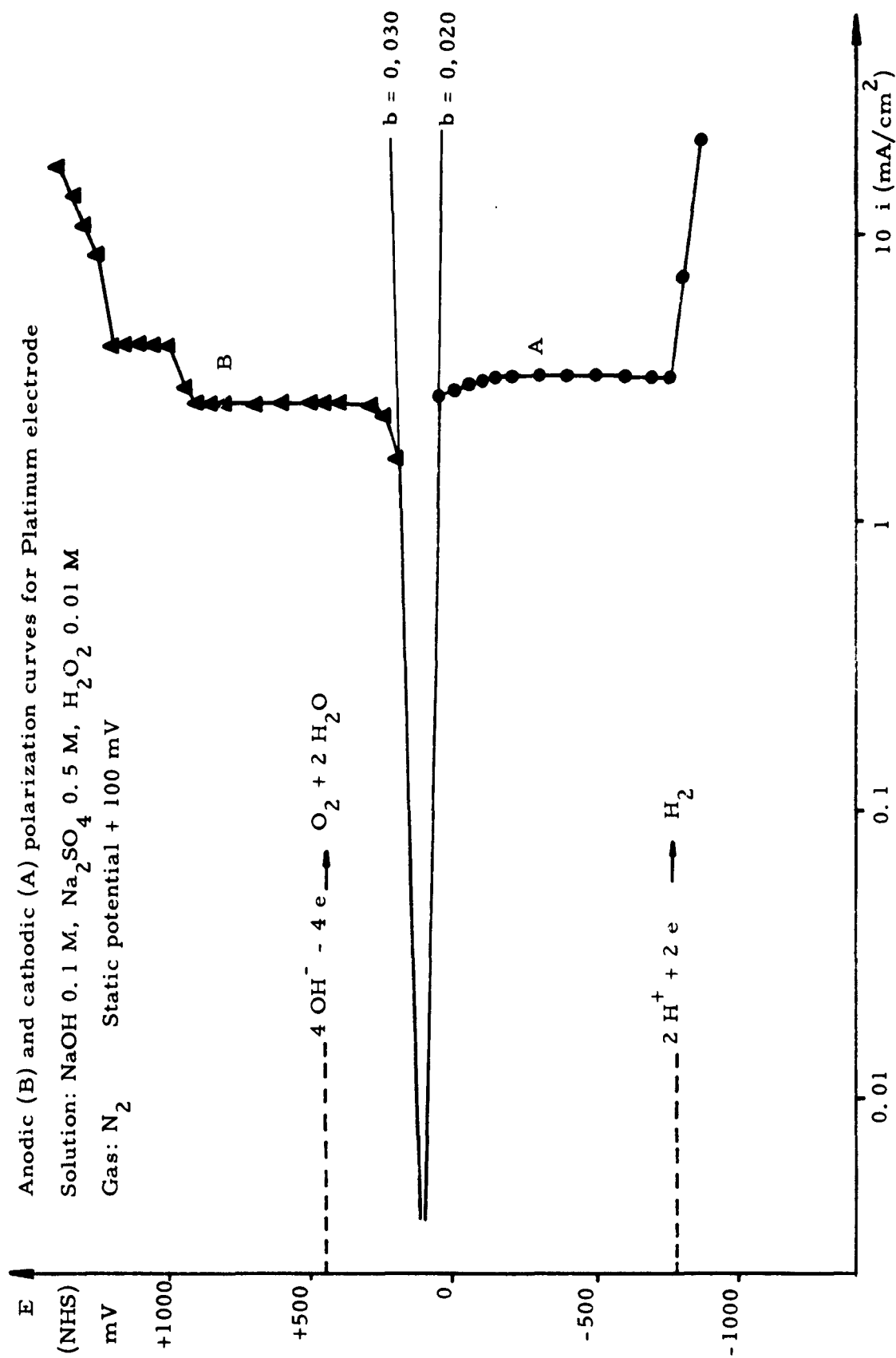Cathodic polarization curve for Platinum electrode

Solution: $\begin{cases} \text{NaOH 0.1 M} \\ \text{Na}_2\text{SO}_4 \text{ 0.5 M} \end{cases}$ gas O_2

Static potential + 200 mV

$b = 0,060$

$2 H^+ + 2 e \longrightarrow H_2$

E (NHS) mV

+1000
+500
0
-500
-1000

0.01   0.1   1   10   i (mA/cm^2)

Fig. 1

Cathodic polarization curve for Palladium electrode

Solution: NaOH 0.1 M, Na_2SO_4 0.05 M; gas O_2

Static potential + 210 mV

b = 0,060

$2 H^+ + 2 e \longrightarrow H_2$

E
(NHS)
mV

+1000

+500

0

-500

-1000

0.01   0.1   1   10   i (mA/cm^2)

Fig. 2

Cathodic polarization curve for Iridium electrode

Solution: NaOH 0.1 M, Na_2SO_4 0.5 M

Gas O_2 Static potential + 230 mV

$2 H^+ + 2 e \longrightarrow H_2$

b = 0,12

10 i (mA/cm^2)

E (NHS) mV

+1000

+500

0

-500

-1000

0.01   0.1   1   10

Fig. 3

Anodic (B) and cathodic (A) polarization curves for Platinum electrode

Solution: NaOH 0.1 M, Na_2SO_4 0.5 M, H_2O_2 0.01 M

Gas: N_2 Static potential + 100 mV

$4\ OH^- - 4\ e \longrightarrow O_2 + 2\ H_2O$

$2\ H^+ + 2\ e \longrightarrow H_2$

b = 0,030

b = 0,020

E
(NHS)
mV

+1000

+500

0

−500

−1000

10 i (mA/cm^2)

0.01   0.1   1

Fig. 4

Cathodic (A) and anodic (B) polarization curves for Palladium electrode

Solution: NaOH 0.1 M, Na$_2$SO$_4$ 0.5 M, H$_2$O$_2$ 0.01 M

Gas: N$_2$; Static potential + 110 mV

Fig. 5

Cathodic (A) and anodic (B) polarization curves for Iridium electrode

Solution: NaOH 0.1 M, Na_2SO_4 0.5 M, H_2O_2 0.01 M

Gas: N_2 Static potential + 150 mV

E
(NHS)
mV

+1000

+500

0

−500

−1000

$b = 0,030$

$b = 0,060$

B

A

$.4\ OH^- - 4\ e \longrightarrow O_2 + 2\ H_2O$

$2\ H^+ + 2\ e \longrightarrow H_2$

0.01   0.1   1   10 $i\ (mA/cm^2)$

Fig. 6

Cathodic polarization curve for Platinum electrode

Solution: Na$_2$SO$_4$ 0.5 M, H$_3$BO$_3$ 0.5 M, NaOH enough to reach pH 7

Gas O$_2$ Static potential + 510 mV

b = 0,060

2 H$^+$ + 2 e ⟶ H$_2$

E (NHS) mV

+1500
+1000
+500
0
-500

0.01   0.1   1   10   i (mA/cm^2)

Fig. 7

Cathodic polarization curve for Palladium electrode

Solution: Na_2SO_4 0.5 M, H_3BO_3 0.5 M, NaOH enough to reach pH 7

Gas: O_2 Static potential + 520 mV

b = 0,060

$2 H^+ + 2 e \longrightarrow H_2$

E (NHS) mV

+1500

+1000

+500

0

-500

0.01   0.1   1   10 i (mA/cm^2)

Fig. 8

Cathodic polarization curve for Iridium electrode

Solution: Na_2SO_4 0.5 M, H_3BO_3 0.5 M, NaOH enough to reach pH 7

Gas: O_2 Static potential + 520 mV

b = 0,160

$2 H^+ + 2 e \longrightarrow H_2$

E (NHS) mV

+1500

+1000

+500

0

−500

0.01   0.1   1   10 i (mA/cm^2)

Fig. 9

Cathodic (A) and anodic (B) polarization curve for Platinum electrode

Solution: Na_2SO_4 0.5 M, H_3BO_3 0.5 M, NaOH enough to reach pH 7, H_2O_2 0.01 M

Gas: N_2 Static potential + 440 mV

b = 0,060

b = 0,030

B

A

$4\ OH^- - 4\ e \longrightarrow O_2 + 2\ H_2O$

$2\ H^+ + 2\ e \longrightarrow H_2$

E (NHS) mV

+1500

+1000

+500

0

-500

0.01

0.1

1

10 i (mA/cm^2)

Fig. 10

Cathodic (A) and anodic (B) polarization curves for Palladium electrode

Solution: Na_2SO_4 0.3 M, H_3BO_3 0.5 M,

NaOH enough to reach pH 7, H_2O_2 0.01 M

Gas: N_2 ; Static potential + 470 mV

$4 OH^- - 4e \longrightarrow O_2 + 2 H_2O$

$2 H^+ + 2e \longrightarrow H_2$

b = 0,020

b = 0,020

B

A

E
(NHS)
mV

+1500

+1000

+500

0

− 500

0.01

0.1

1

10 i (mA/cm^2)

Fig. 11

Cathodic (A) and anodic (B) polarization curves for Iridium electrode

Solution: Na_2SO_4 0.5 M, H_3BO_3 0 5 M, NaOH enough to reach pH 7, H_2O_2 0.01 M

Gas: N_2 Static potential + 460 mV

$$4\,OH^- - 4\,e \longrightarrow O_2 + 2\,H_2O$$

$$2\,H^+ + 2\,e \longrightarrow H_2$$

b = 0,040

b = 0,42

A

B

E
(NHS)
mV

+1500

+1000

+500

0

-500

10 i (mA/cm^2)

0.01

0.1

1

2

Fig. 12

Cathodic polarization curves for Platinum electrode

Solutions: H$_2$SO$_4$ 0.5 M, curve A: static potential + 920 mV

HCl M,　curve B :　static potential + 720 mV

Gas: O$_2$

E
(NHS)
mV

+2000

+1500

+1000

+500

0

A

B

b = 0.060

b = 0.180

2 H$^+$ + 2 e $\longrightarrow$ H$_2$

0.01　0.1　1　10 i (mA/cm^2)

Fig. 13

Platinum electrode

A : cathodic polarization curve - solution: H_2SO_4 0.5 M, H_2O_2 0.01 M; gas N_2

B : cathodic polarization curve - solution: HCl M, H_2O_2 0.01 M; gas N_2

C : anodic polarization curve - solution: H_2SO_4 0.5 M, H_2O_2 0.01 M, gas N_2

$$4\,OH^- - 4\,e \longrightarrow O_2 + 2\,H_2O$$

$$2\,H^+ + 2\,e \longrightarrow H_2$$

b = 0,080

b = 0,240

Fig. 14

Cathodic polarization curves for Iridium electrode

Solutions: H_2SO_4 0.5 M, curve A: static potential + 900 mV

HCl M, curve B: static potential + 855 mV

Gas: O_2

Fig. 15

Iridium electrode

A : cathodic polarization curve - solution: H_2SO_4 0.5 M, H_2O_2 0.01 M; gas N_2

B : cathodic polarization curve - solution: HCl M, H_2O_2 0.01 M; gas N_2

C : anodic polarization curve - solution: H_2SO_4 0.5 M, H_2O_2 0.01 M; gas N_2

$4OH^- - 4 e \longrightarrow O_2 + 2 H_2O$

$2 H^+ + 2 e \longrightarrow H_2$

b = 0,050

b = 0,34

C

A

B

E (NHS) mV

+2000

+1500

+1000

+500

0

0.01

0.1

1

10 i (mA/cm^2)

Fig. 16

Cathodic polarization curves for Platinum - 10% Iridium electrode

Solutions: H_2SO_4 0.5 M, curve A : static potential + 900 mV
HCl M, curve B : static potential + 850 mV

Gas: O_2

Fig. 17

Cathodic polarization curves for Pt - 10% Iridium electrode

Solutions: H_2SO_4 0.5 M, H_2O_2 0.01 M, curve A: static potential + 790 mV

HCl M, H_2O_2 0.01 M, curve B: static potential + 840 mV

Gas: N_2

E (NHS) mV

+2000

+1500

+1000

+500

0

A

B

b = 0,40

b = 0,45

$2 H^+ + 2 e \longrightarrow H_2$

0.01   0.1   1   10 i (mA/cm^2)

Fig. 18

Cathodic polarization curves for Platinum - 20% Iridium electrode

Solutions: H_2SO_4 0 5 M, curve A : static potential + 900 mV

HCl M,   curve B: static potential + 850 mV

b = 0,100

b = 0,190

A

B

$2 H^+ + 2 e \longrightarrow H_2$

E
(NHS)
mV

+2000

+1500

+1000

+500

0

0.01

0.1

1

10 i (mA/cm^2)

Fig. 19

Cathodic polarization curves for Platinum - 20% Iridium electrode

Solutions: curve A : H_2SO_4 0.5 M, H_2O_2 0.01 M; static potential + 790 mV

curve B : HCl M, H_2O_2 0.01 M; static potential + 860 mV

Gas: N_2

Fig. 20

Cathodic polarization curve for Palladium electrode

Solution: H_2SO_4 0.5 M

Gas: O_2 Static potential + 770 mV

$2 H^+ + 2 e \longrightarrow H_2$

E (NHS) mV

+2000

+1500

+1000

+500

0

0.01   0.1   1   10 i (mA/cm^2)

Fig. 21

Anodic (A) and cathodic (B) polarization curves for Palladium electrode

Solution: H_2SO_4 0,5 M; H_2O_2 0,01 M

Gas: N_2 ; Static potential + 780 mV

$4OH^- - 4e \longrightarrow O_2 + 2H_2O$

$2H^+ + 2e \longrightarrow H_2$

b = 0,060

b = 0,24

A

B

E (NHS) mV

+2000

+1500

+1000

+500

0

0.01

0.1

1

10 i (mA/cm²)

Fig. 22

AFOSR 2050

University of Milano (Italy)
Dept. of Electrochemistry
and Metallurgy
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"CATHODIC REDUCTION OF O_2 AND H_2O_2 ON Pt, Pd AND Ir SMOOTH ELECTRODES"
by G. Bianchi, F. Mazza and T. Mussini; December 1961

ABSTRACT / Polarization curves in acid, neutral and alkaline solutions have been drawn by potentiostatic method, for O_2 and H_2O_2 reduction processes and for H_2O_2 oxidation process on Pt, Ir and Pd electrodes. These curves could be classified as follows: those whose slopes are 0.03 to 0.12, and those with slopes higher than 0.12. The former can be explained through already proposed mechanisms (addition of one electron or one atom of hydrogen to an adsorbed oxygen molecule; or addition of one electron to an HO_2 adsorbed radical) which

mechanisms imply that the adsorption process is so quick as not to result kinetically determining. The latter involve a slow oxygen or HO$_2$-radical adsorption which becomes kinetically determining, first of all for Iridium in both acid and neutral solutions. For Palladium in H$_2$SO$_4$ solutions and for Platinum in HCl solutions the oxygen adsorption process is very slow essentially due to the complexing action of the solution with resulting formation of surface complexes which engage the metal atoms, thus preventing or reducing the formation of adsorbed oxide.